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The Si ribbon crystal for the solar battery using the horizontal pull method.

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PREFACE

In 1969, C. E. Bleil of G. M. applied the horizontal pull method to crystal growth of ice and germanium. In order to remove the heat from coagulation in the growth site, solid materials directly in contact with the crystal surface were used for cooling. There was uneven cooling due to the imperfect contact among the solid materials themselves and as a result there was a problem in the dimensional precision of the wafer-like crystal. Furthermore, materials like silicon with a high melting point and active chemical reactions at high temperature were found difficult to use. The rate of growth was also slow. As a part of the Sunshine Plan, (Research and Development of the Solar Ray Electricity Generation System), the silicon horizontal pulling ribbon crystal growth method has been researched and developed. Basically, it is a new version of the Bleil method. Figure 1 shows the principle of the silicon horizontal pulling system. The salient points in the method are that, by applying some sort of device to spray noble gases to cool the site of growth, (1) soft and uniform cooling was possible, (2) the length of the boundary surface of growth along the growth direction was made long over a wide width compared to the thickness, and (3) this made it possible to effectively remove the heat produced from solidification. By using forced gas spraying on the solution surface in contact with the points of crystal growth, growth at the points of growth can be enhanced and the rate of growth can be speeded up.

HISTORY OF THE RESEARCH

This research began in 1974. During 1974, an initial stage growth machine system, Machine Number One, for the high frequency heating batch system was devised to conduct the tests for crystal growth. Using this machine, in 1974, 200 mm/min and in 1975, 415 mm/min single crystal high speed pulling rates were experienced. This was followed by a change of the heating system to a resistance heating system and by Machine Number Two with an additional number of heaters added to it. From the test, using a rectangular shallow bottom melting pot of the Machine Number Two, one could see that the grown crystal in the shallow bottom melting pot was a tree branch shaped crystal. On the basis of the results obtained the year before, during 1976, Machine Number Three (Photo 1) which is equipped with a continuous process mechanism was built (a continuous charging mechanism outside the raw material furnace, a pulling out mechanism for growing crystals outside the continuous furnace). Testing was started for practical applications. Evaluation of all the characteristic properties of the silicon horizontal pulling ribbon crystal showed that it has about the same qualities as the traditional C Z crystal method. The photoelectric conversion efficiency is 7.8% with the test solar battery using the "lap basic panel" ribbon crystal. (This is equivalent to 10.9% in case the reflection prevention membrane is used). Since 1977, based on research so far (see Table 1), developmental research has been concentrated on the establishment of a balanced continuous pulling method using Test Machine Number Three equipped with a furnace interior structure which made use of the deep bottom melting pot (Photo 1).

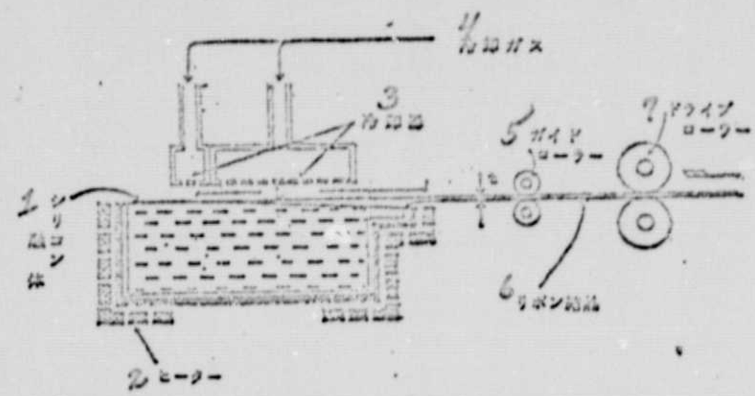


Figure 1. The principal of the silicon horizontal pull method.

Key: 1 - silicon fluids; 2 - heater; 3 - cooling device; 4 - gas collant; 5 - guide roller; 6 - ribbon crystal; 7 - drive roller

CONCENTRATION OF THE RESEARCH AND RESULTS

The undesirable phenomena which affect the balanced continuous pulling out method are as follows:

(1) Development of recrystals.

1) Bridge at the point of pulling out (Fig. 2)..

a) Bridge of the beginning stage.

This is a bridging phenomenon between the recrystal developed at the point of pulling out during the beginning stage of operation and along the rear part of the growth boundary surface as it is being pulled out.

b) Growth bridge.

This is phenomenon in which a stalagmite from the bottom of the meniscus gradually bridges over the crystal being pulled out.

2) Peripheral recrystallization (top and side single crystal) (Fig. 3).

In this phenomenon, as the crystal is being pulled out, the recrystal develops at the top and around the side bridges over to the growth boundary surface because of the increased volume of cooling gas.

(2) Vertical-downward growth -->droppings (Fig. 4).

This is a phenomenon in which, from the initial operation up to the pulling out operation, the growth boundary surface develops in the direction of depth and finally the liquid drops.

(3) Polycrystallization (Fig. 5).

In case floating matter develops during the melting process and it is not removed from the seed, the growth surface of the seed remains impure and the grown crystal becomes a polycrystal. Also, if the cooling is too fast, it becomes a tree branch shaped cristal.

(4) The growth chip (Fig. 6).

In case the increase in the cooling gas is not enough in comparison to the increase of the crystal pulling rate, the growth boundary surface spreads poorly and a "growth chip" develops.

One particularly important problem to be overcome for the balanced continuous pulling out is to control the recrystallization around the circumference of the melting pot. In expectation of a successful control of the circumference recrystallization development and stabilization of the growth site, the size of the pulling out melting pot was made large (82ϕ --> 120ϕ). Also, the test has been repeated in order to normalize the structure of the pulling out bath heater, the supplementary heater and normalization of the power balance. The cooling gas amount, the rate of pulling out, the heating power of the heater, etc., were coordinated following the program for normalization. The direction for long size production was verified. In 1977, using the above mentioned methods of operation, a ribbon crystal longer than 700 mm was produced and in 1978 a ribbon single crystal longer than 5,000 mm was produced. Figure 7 shows the furnace interior structure of the deep bottom melting pot system for Machine Number Three.

The result from the evaluation of the crystal characteristics and the result from the measurement of the test solar battery characteristics showed that the long size ribbon also has a same quality as the traditional single crystal. Figure 8 shows an example of the V-1 characteristic of the test solar battery. (The ribbon crystal lap basic wafer was used). Figure 9 shows the distribution of the growth direction resistance rate of the long size ribbon crystal.

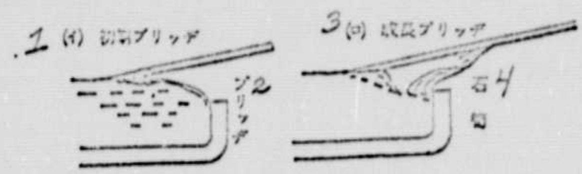


Figure 2. Bridge at the point of pulling out

Key: 1(a) - bridge of the beginning stage; 2 - bridge; 3(b) - growth bridge; 4 - stalagmite

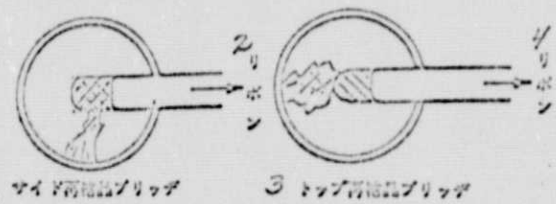


Figure 3. Peripheral recrystallization

Key: 1 - side recrystallization bridge; 2 - ribbon; 3 - top recrystallation bridge; 4- ribbon

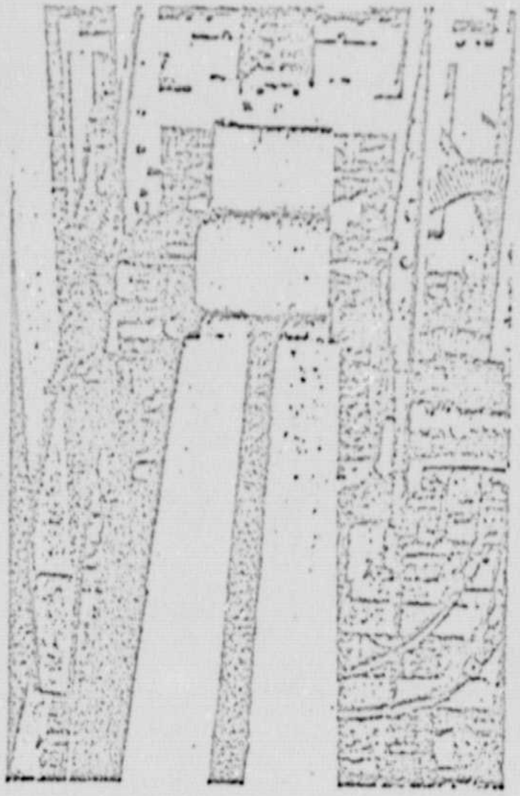


Photo 1. Pulling out a long ribbon from Test Machine Number Three

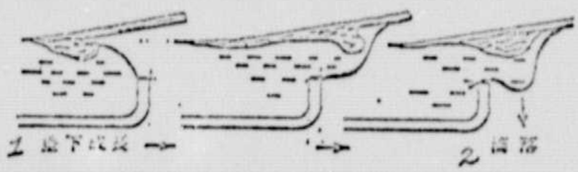


Figure 4. Vertical-downward growth--dropping

Key: 1 - vertical-downward growth; 2 - dropping

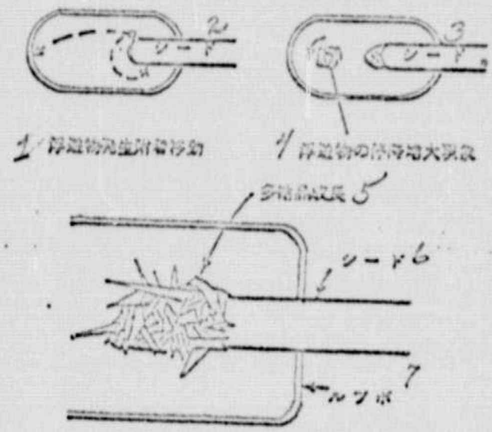


Figure 5. Floating matter and polycrystallization growth

Key: 1 - floating matter development; 2 - seed; 3 - seed; 4 - phenomenon of stagnant floating matter and its enlargement; 5 - polycrystallization growth; 6 - seed; 7 - melting pot

Figure 6. Growth chip

Key: 1 - ribbon; 2 - point of growth chip

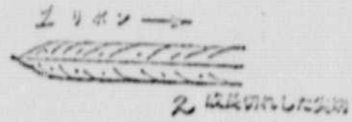
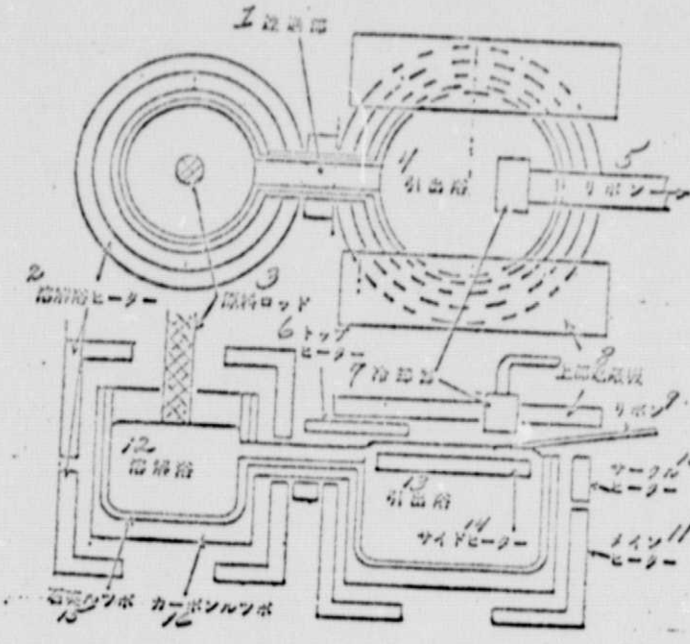
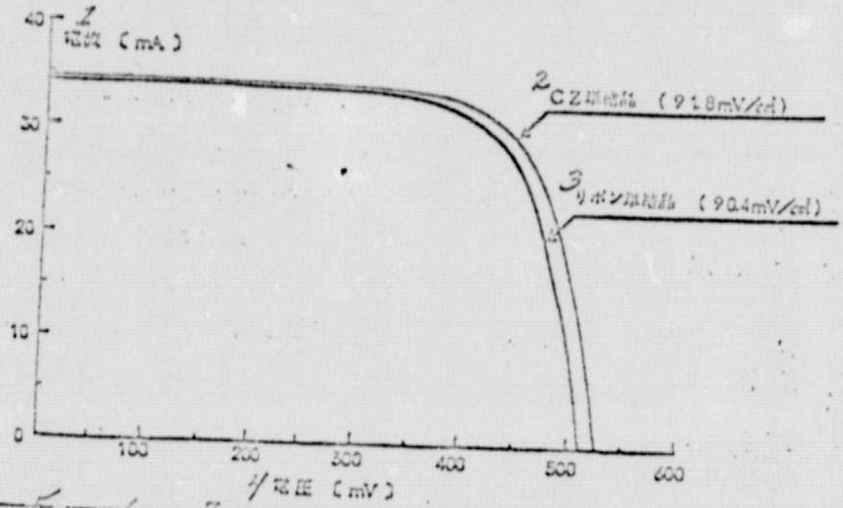


Figure 7. Furnace interior of Machine Number Three

Key: 1 - connecting part; 2 - solution bath heater; 3 - raw material rod; 4 - pulling out bath; 5 - ribbon; 6 - top heater; 7 - cooler; 8 - top screen; 9 - ribbon; 10 - circular heater; 11 - main heater; 12 - solution bath; 13 - pulling out bath; 14 - side heater; 15 - quartz melting pot; 16 - carbon melting pot





5 [illegible]	6 [illegible]	7 [illegible]	Isc	Voc	Wmax	F. F.	η	η×1.4
8 リボン単結晶	1.8 ㎠	904 mW/㎠	340 mA	510 mV	127 mW	0.732	7.8%	10.9%
9 CZ単結晶	1.8	918	345	525	135	0.745	8.2	11.5%

10 測定データーは反射防止膜なしの値

Figure 8. The V-l characteristics of the test solar battery

Key: 1 - electric current; 2 - CZ single crystal; 3 - ribbon single crystal; 4 - electric voltage; 5 - The values are the measured data without the reflection preventive membrane; 6 - Solar battery basic wafer; 7 - Effective area for solar heat; 8 - Density of solar energy; 9 - Ribbon single crystal; 10 - CZ single crystal

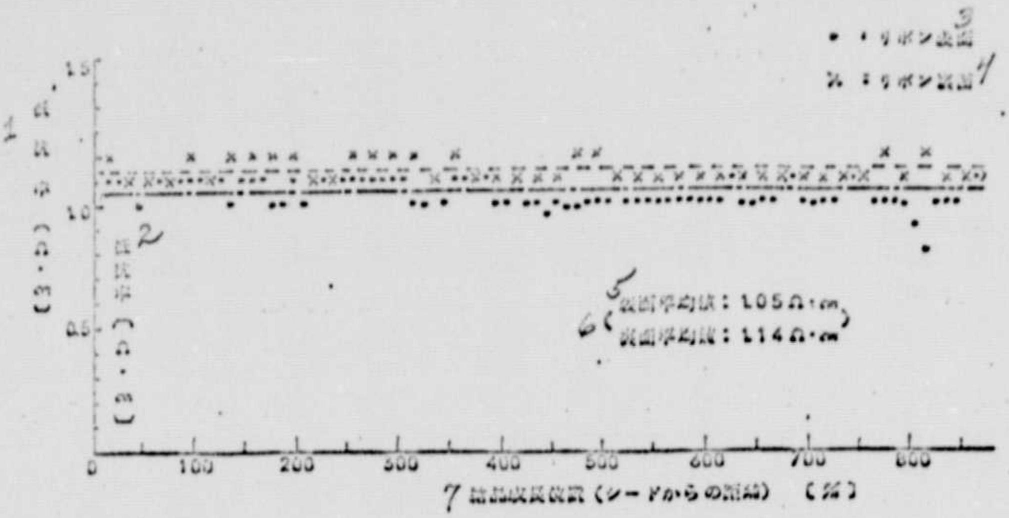


Figure 9. Distribution of growth direction resistance rate of P-type ribbon crystal (Four-needle sounding method)

Key: resistance rate; 2 - resistance rate; 3 - front side of the ribbon; 4 - rear side of the ribbon; 5 - average value of the front side; 6 - average value of the rear side; 7 - crystal growth position (distance from the seed)

FUTURE PROBLEMS

Future problems include prevention of crystal bending caused by the "sway" during the pulling out operation for the long ribbon, how to make the ribbon width wide in order to increase the speed of growth and obtain a wider area (for the ribbon), how to make a thinner wafer by higher speed, and how to improve the dimensional measurement precision.